Intramolecular Spin Alignment Utilizing the Excited Molecular Field between the Triplet ($S = 1$) Excited State and the Dangling Stable Radicals ($S = 1/2$) as Studied by Time-Resolved Electron Spin Resonance: Observation of the Excited Quartet ($S = 3/2$) and Quintet ($S = 2$) States on the Purely Organic π-Conjugated Spin Systems

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Intramolecular spin alignment through π-conjugation in purely organic spin systems is quite important in the field of molecule-based magnetism.[1] Such studies are, however, almost limited to the ground states. The studies on the spin alignment between the stable radicals ($S = 1/2$) and the metastable excited triplet state ($S = 1$) will give very important information on the novel spin alignment, and this leads to a new strategy for the photoinduced/switching magnetic spin systems. In this paper we report the purely organic excited quartet ($S = 3/2$) and quintet ($S = 2$) states originating from such spin alignment in the π-conjugated spin systems. There are only a few examples of the direct observation of such excited high spin ($S \geq 3/2$) states arising from a radical-triplet pair so far reported in the solid phase. One is fullerene linked to nitroxide radical[2,3] and the other is tetraphenylporphilinatozinc(II) (ZnTPP) coordinated by *p*-pyridyl nitronyl nitroxide (nitpy) and its homologues.[4] In the fullerene systems the stable nitroxide radicals couple with the fullerene moiety through σ bonds. We report here the first quartet and quintet excited spin states of the purely organic ***π-conjugated*** spin systems in which strong exchange interaction is expected.

We have chosen phenylanthracene derivatives as the spin coupler and iminonitroxide radical as the dangling stable radicals as shown by 9-[4-(4,4,5,5-tetramethyl-1-yloxyimidazolin-2-yl)-phenyl]anthracene (**1**) and 9,10-bis[4-(4,4,5,5-tetramethyl-1-yloxyimidazolin-2-yl)phenyl]anthracene (**2**) (see Figures 1 and 2).[5] As described later, the phenylanthracene moiety is a suitable photocoupler which gives a ferromagnetic exchange interaction with the dangling iminonitroxide radicals. This leads to the excited quartet state for **1** and the excited quintet state for **2**. To clarify this spin alignment, we have detected the excited high-spin states by using time-resolved electron spin resonance (TRESR) in a rigid glass matrix.

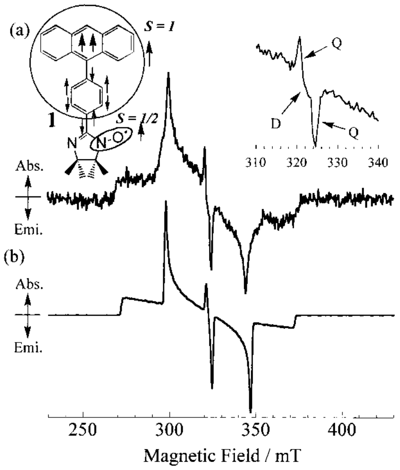

Figure 1. Typical TRESR spectra of **1** in an EPA rigid glass matrix. (a) The observed spectrum at 1.0 μs after laser excitation at 30 K. The inset shows the expanded spectrum in the $g \sim 2$ region. In the inset Q and D denote the signals due to the excited quartet and doublet states, respectively. The molecular structure of **1** and the intramolecular spin alignment expected based on the π-topological rule of the spin correlation (arrows) are also shown. (b) The simulation of the excited quartet spectrum using the spin Hamiltonian parameters described in the text (line width 0.7 mT).

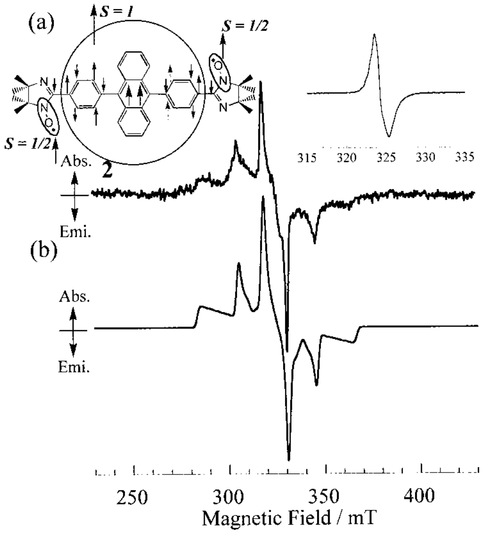

Figure 2. Typical TRESR spectra of **2** in a 2MTHF rigid glass matrix. (a) The observed spectrum at 1.0 μs after laser excitation at 30 K. The observed TRESR shows an absorption (A) and an emission (E) of the microwave at the lower magnetic field and higher magnetic field sides (A/E pattern). The inset shows the ordinary ESR spectrum before laser excitation. (b) The simulation of the excited quintet spectrum using the spin Hamiltonian parameters described in the text (line width 0.7 mT).

A conventional ESR spectrometer (JEOL TE300) was modified for the TRESR experiments. The photoexcitation was carried out at 355 nm using a YAG laser. EPA and 2MTHF glass matrices were used for the experiments.

A typical TRESR spectrum of **1** observed at 1.0 μs after the laser excitation at 30 K is shown in Figure 1, together with simulation. The simulation was carried out by the eigenfield/exact-diagonalization hybrid method,[6,7] taking electron spin polarization (ESP) into account. Since the effective-exchange interaction between the triplet state and radical is undoubtedly much larger

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(5) **1**: mp 190−193 °C. Anal. Calcd for $C_{27}H_{25}N_2O$: C, 82.41; H, 6.40; N, 7.12. Found: C, 82.17; H, 6.46; N, 7.01. **2**: mp >300 °C. Anal. Calcd for $C_{40}H_{40}N_4O_2{\cdot}H_2O$: C, 76.65; H, 6.75; N, 8.94. Found: C, 76.69; H, 6.63; N, 8.73.

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than the Zeeman and fine-structure interactions in the present π-conjugated systems, we used the ordinary spin Hamiltonian of the pure spin state which is given by

$$\begin{aligned} H'_{\text{spin}} &= \beta_e \boldsymbol{H}\cdot\boldsymbol{g}\cdot\boldsymbol{S} + \boldsymbol{S}\cdot\boldsymbol{D}\cdot\boldsymbol{S} \\ &= \beta_e \boldsymbol{H}\cdot\boldsymbol{g}\cdot\boldsymbol{S} + D[S_Z{}^2 - S(S+1)/3] + E(S_X{}^2 - S_Y{}^2) \end{aligned} \tag{1}$$

The spin Hamiltonian parameters determined by the spectral simulation are $S = 3/2$, $D = 0.0235\ \text{cm}^{-1}$, $E = 0.0\ \text{cm}^{-1}$, and $g = 2.0043$. In this system the triplet state of the phenylanthracene moiety couples weakly with the dangling stable radical. In this weakly interacting case, the g and D values for the quartet (Q) and doublet (D) states of the triplet−doublet pair are given by[8]

$$\begin{aligned} g(\text{Q}) &= (2/3)g(\text{T}) + (1/3)g(\text{R}) \\ g(\text{D}) &= (4/3)g(\text{T}) - (1/3)g(\text{R}) \end{aligned} \tag{2}$$

and

$$D(\text{Q}) = (1/3)(D(\text{T}) + D(\text{RT})) \tag{3}$$

From the equations, the g value for the excited quartet state of **1** can be estimated to be $g(\text{Q}) = 2.0043$ using the g values of 2.007 and of 2.003 for the nitroxide radical and the triplet excited state of free anthracene. The fine-structure parameter D for the excited quartet state is also estimated to be $D(\text{Q}) = 0.0256\ \text{cm}^{-1}$ using $D(\text{T}) = 0.0710\ \text{cm}^{-1}$ for the triplet excited state of anthracene and $D(\text{RT}) = 0.0057\ \text{cm}^{-1}$ calculated by a point dipole approximation. In this estimation, we used the g and D values of anthracene since those of phenylanthracene are unknown.[9] The experimentally determined g and D values of **1** agree well with the estimations. This shows that the observed excited quartet state arises from the triplet excited state of phenylanthracene and dangling radical spin. The relative populations (polarization) of each M_S sublevel in Q have been determined to be $P_{1/2'} = P_{-1/2'} = 0.5$ and $P_{3/2'} = P_{-3/2'} = 0.0$ with an increasing order of energy in zero magnetic field from the spectral simulation.[10] This ESP can be well interpreted by assuming the selective intersystem crossing (ISC) ($D_1 \rightarrow Q$) which is generated by spin−orbit coupling (SOC) between the excited quartet and the excited doublet states in a manner similar to the case of ZnTPP-nitpy.[4b]

The signal with emissive polarization (E) due to the excited doublet spin state was very weakly detected (see the inset in Figure 1a), indicating that the energy location of the quartet state is lower than that of the excited doublet state and that the sign of the exchange interaction would be positive (ferromagnetic) between the excited triplet state ($S = 1$) of the phenylanthracene moiety and the doublet spin ($S = 1/2$) of the dangling radical. The very weak intensity of the doublet state compared with that of ZnTPP-nitpy can be accounted for in terms of the expected large energy separation between the quartet and doublet states due to the larger exchange interaction arising from the π-conjugation since the ESP of the excited doublet state arises from the perturbed mixing between the quartet and doublet wave functions. These findings agree with the topological nature[11,12] of the spin correlation in the ground state of π-conjugated high-spin systems, as indicated by arrows in Figure 1a. Accordingly, this shows that the π-topological rule of the spin polarization established for the ground-state hydrocarbons also works well in the excited states.

A typical TRESR spectrum of **2** observed at 1.0 μs after the laser excitation at 30 K is shown in Figure 2, together with simulation. The spin Hamiltonian parameters determined are $S = 2$, $D = 0.0130\ \text{cm}^{-1}$, $E = 0.0\ \text{cm}^{-1}$, and $g = 2.0043$. According to the projection theorem of the angular momentum,[13] the D value for the quintet state (Qu) arising from the weakly interacting triplet and two doublet spin states is given by

$$D(\text{Qu}) = (1/6)(D(\text{T}) + D(\text{R}_1\text{T}) + D(\text{R}_2\text{T})) \tag{4}$$

The D value for the excited quintet state is estimated to be $D(\text{Qu}) = 0.0137\ \text{cm}^{-1}$ from eq 4 in the same manner as for **1**.[14] The experimentally determined D value ($0.0130\ \text{cm}^{-1}$) for the excited quintet state of **2** agrees well with the estimation, showing that the observed excited quintet state ($S = 2$) arises from the triplet excited state of the diphenylanthracene moiety and two dangling radical spins. The relative populations of each M_S sublevel have been determined to be $P_{0'} = 0.30$, $P_{-1'} = P_{1'} = 0.35$, and $P_{-2'} = P_{+2'} = 0.0$ in the zero magnetic field. In the same manner as for the quartet states of **1**, the ESP pattern can be interpreted by a selective ISC ($S_1 \rightarrow \text{Qu}$) which is generated through SOC between the eigenfunctions of the excited quintet state and excited singlet states.

The direct detection of the quintet TRESR spectrum with well-resolved fine-structure splitting shows that a strong ferromagnetic (parallel) exchange interaction between the two dangling radicals ($S = 1/2$) can be realized in the photoexcited state through the triplet excited spin-coupler ($S = 1$) of diphenylanthracene. On the other hand, in the ground state two dangling radicals have almost no exchange interaction; the ordinary ESR spectrum of **2** shows the typical fine-structure less spectral pattern (the inset of Figure 2a).[15] There are two dominant mechanisms for the intramolecular spin alignment. One is the spin polarization mechanism and the other is the spin delocalization mechanism.[16] In the ground state of the closed shell spin coupler, the former mechanism is dominant compared with the latter as established.[11,12] Since **2** is a symmetrical diradical, the spin poralization mechanism leads to the antiferromagnetic (antiparallel) spin configuration between the dangling radicals in the ground state, according to the topological rule of the π-electron network.[11,12] On the other hand, in the open-shell T_1 state of the anthracene moiety the spin delocalization mechanism is dominant. This leads to a large positive spin density with the same sign at the 9 and 10 positions of the anthracene moiety. The ferromagnetic (parallel) spin configuration will therefore be realized through spin polarization by the π-conjugation as shown by arrows in Figure 2a. These results show that the sign of the exchange interaction can be changed from antiferromagnetic to ferromagnetic by the photoexcitation.

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(9) The g, D, and E values for the T_1 state of anthracene in the EPA rigid glass matrix have been determined to be $g = 2.003$, $D = 0.0710\ \text{cm}^{-1}$, and $E = 0.0070\ \text{cm}^{-1}$ as well as $P_X = 0.45$, $P_Y = 0.55$, and $P_Z = 0.0$. Since the π spin density on phenyl or diphenylanthracene is slightly delocalized to the phenyl rings, the D will be slightly reduced.

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